

Spin-polarized core-level photoemission of oxidized Fe(001)(invited)

B. Sinkovic

Department of Physics, New York University, 2 Washington Place, New York, New York 10003

P. D. Johnson and N. B. Brookes

Physics Department, Brookhaven National Laboratory, Upton, New York 11973-5000

A. Clarke and N. V. Smith

AT & T Bell Laboratories, Murray Hill, New Jersey 17974-2070

The combination of spin-polarization detection with core-level photoemission to give spin-polarized electron spectroscopy for chemical analysis provides new information on the oxidation of an iron surface. During the initial stage of oxidation the predominant phase is of a ferrimagnetic γ -Fe₂O₃ form. The observed antiferromagnetic coupling of this oxide with the iron substrate is attributed to the superexchange interaction mediated by an oxygen ion. This provides evidence for a site exchange mechanism during the initial oxidation. Annealing transforms this oxide into an antiferromagnetic Fe_xO form which is also present at the initial stage.

I. INTRODUCTION

Studies of magnetism at surfaces and thin films with techniques involving spin-polarized electrons are becoming increasingly commonplace.^{1,2} In particular, spin-polarized photoemission has been recognized as a powerful tool for study of the electronic structure of ferromagnetic materials³ and their interaction with impurity atoms.⁴ The majority of these studies⁵ have, however, concentrated on photoemission from the valence bands which tend to reflect delocalized properties. By combining spin-polarization analysis with chemical sensitivity of core-level photoemission, here we demonstrate the potential of a new probe, spin-polarized electron spectroscopy for chemical analysis (SPESCA).

The system studied is initial oxidation of an iron surface. Iron oxides naturally occur in four forms that differ in structure, chemical composition, and magnetic properties. They are: Antiferromagnetic FeO (NaCl structure; Fe²⁺ ions) and α -Fe₂O₃ (corundum structure; Fe³⁺ ions), and ferrimagnetic γ -Fe₂O₃ (inverse spinel structure; Fe³⁺ ions) and Fe₃O₄ (inverse spinel structure; Fe²⁺ and Fe³⁺ ions). There have been a number of earlier studies of iron oxidation⁶⁻⁸ but without measurement of the magnetic properties. It is agreed that the chemisorption at low oxygen exposures is followed by the formation of a predominantly γ -Fe₂O₃-like oxide. An early x-ray photoemission (XPS) study⁶ of the Fe 2*p* level following the initial oxidation of polycrystalline iron found evidence of both Fe³⁺ and Fe²⁺ states. Fe²⁺ would suggest the presence of FeO, Fe³⁺ would be consistent with the presence of either α -Fe₂O₃ or γ -Fe₂O₃, and a mixture of Fe³⁺ and Fe²⁺ would point to Fe₃O₄ and/or mixture of FeO and both α - and γ -Fe₂O₃. A spin-polarized Auger electron spectroscopy study⁷ of the oxidation of Fe(001) concluded that chemisorption at low exposure was followed by the forma-

tion of γ -Fe₂O₃-type oxide at the saturation exposures. This was in agreement with an earlier electron energy loss spectroscopy⁸ (EELS) study which also indicated that there is a distinct oxide phase following chemisorption and proceeding the final oxide formation. It was proposed that that phase represents a two-dimensional thin oxide formed by oxygen incorporation into the Fe lattice. However, the exact composition, structure, and magnetic properties of this initial oxide phase were unknown. The present studies combining spin analysis and core-level photoemission techniques provide new information on this phase. The experiment reveals evidence for, within the initial oxidation, the presence of a ferro- or ferrimagnetic oxide phase which couples antiferromagnetically to the iron substrate. Annealing the surface leads to the formation of an oxide showing a smaller core-level shift and a loss of polarization. The latter observation suggests that the final oxide state is either paramagnetic or antiferromagnetic.

II. EXPERIMENTAL METHOD

The experiments were carried out on a system that has been described extensively elsewhere.⁹ Briefly, photons are provided by the UV undulator installed on the VUV ring at the NSLS. The photoemitted electrons are detected by a hemispherical analyzer equipped with a low-energy spin detector, the latter described in more detail elsewhere.¹⁰ The estimated angular resolution is $\pm 1.5^\circ$ and the estimated overall energy resolution (from both the photon monochromator and the electron energy analyzer) is 0.5 eV. All measurements are made with a single-crystal Fe "picture-frame" sample¹¹ in remanent magnetization. Following cycles of argon bombardment and annealing to produce a clean sample, the oxidation studies were performed by exposing the sample to oxygen. Low-energy electron diffraction (LEED) and Auger electron spectroscopy were

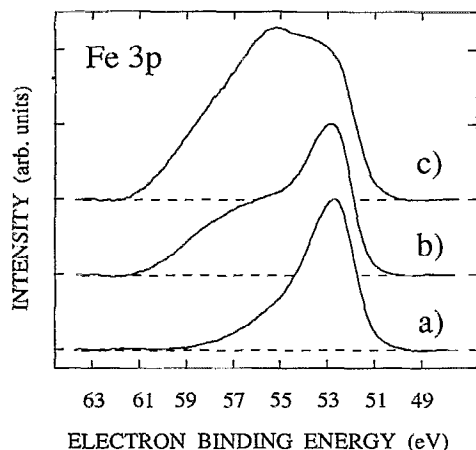


FIG. 1. Spin-integrated Fe 3p photoemission spectra (after background subtraction) taken during the initial oxidation of Fe(001). (a) Clean surface, (b) after exposure to 16 L of O₂, (c) after exposure to 16 L of O₂ and subsequent annealing to 650 °C.

provided to monitor the crystal order and surface cleanliness, respectively. All the photoelectron spectra shown here were recorded at room temperature using photons of 90 eV energy.

III. RESULTS

The spin-integrated core-level photoemission or electron spectroscopy for chemical analysis (ESCA) has been proven in the past as a powerful technique for study of chemical composition in the surface region. In Figs. 1(a)–1(c) we show Fe 3p photoemission spectra (background subtracted) during the initial oxidation of the Fe(001) surface. The spectrum from a clean surface [Fig. 1(a)] shows asymmetric, Doniach–Sunjic¹² line-shape characteristic of photoemission from metallic materials. An identical spectrum is observed after exposing the iron crystal to 6 L [1 langmuir (L) = 10^{−6} Torr for 1 s] of oxygen. This chemisorbed phase is characterized by observation of a $p(1 \times 1)$ surface structure in LEED, and is not expected to make an observable change in the Fe 3p spectrum due to relatively small interaction of Fe and O atoms. Further oxygen exposure initiates the oxidation process. This is detected in the Fe 3p photoemission spectrum [Fig. 1(b)] as a development of a strong shoulder at a binding energy of about 4.5 eV above the metal peak. The shoulder corresponds to initial iron oxide and is associated with Fe³⁺ or Fe³⁺ plus Fe²⁺ species in agreement with previous study.⁶ Further oxygen exposure increases a component of spectral intensity assigned to the oxides indicating formation of thicker oxides. An interesting transformation of the initial oxide is observed upon annealing the sample to 650 °C. The Fe 3p spectrum of this phase [Fig. 1(c)] shows changes that suggest not only an increase in oxide concentration but also a change in its chemical composition (shift to lower binding energy).

In the remainder of this paper we discuss spin-resolved aspects of the three spectra shown in Fig. 1. It is demonstrated how such a spin-polarized electron spectroscopy for

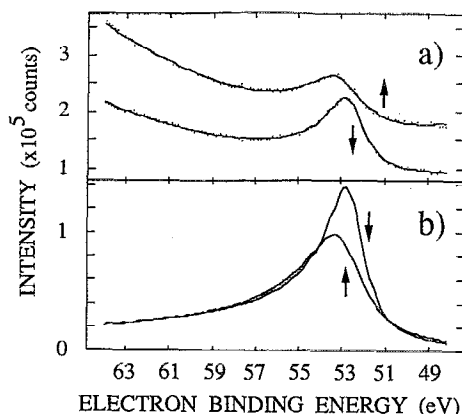


FIG. 2. (a) Spin-resolved Fe 3p photoemission spectra recorded from clean Fe(001) with 90-eV photons. Also shown (full lines) are Doniach–Sunjic curves fitted to the data. (b) Doniach–Sunjic curves for two spin components without the background.

chemical analysis (SPESCA) can be used to provide information on the magnetic properties during the oxidation process. In order to prove that core-level photoemission from magnetic materials is spin dependent, and thus can be used to study magnetism, we first briefly concentrate on clean Fe(001). Here we repeat an earlier spin-polarized photoemission study of the iron 3p level.¹³ Figure 2(a) shows majority and minority Fe 3p spectra together with their fits (full curve) to a Doniach–Sunjic¹² line shape plus a background. The fitted curves without the background are shown in Fig. 2(b). In contrast to the earlier study, we find that the two spin components have nearly identical line shape (peak asymmetry of 0.31). Their widths, on the other hand, are rather different (2.7 eV for the majority component and 1.7 eV for minority) as reported previously. The two spectra are exchange split by 0.5 eV with the more intense minority peak at lower binding energy. The spin polarization in the core level is −23%. These observations can be naively explained within the atomic multiplet theory.^{14–16} The relative intensity of the two spin components is consistent with multiplicity arguments for the respective final states ⁵P and ⁷P. This simple theory also explains the observation of the ⁷P-like final state at lower binding energy than the ⁵P state. However, the atomic multiplet theory cannot be straightforwardly applied to metallic systems (it has been very successful in explaining the spectra of transition metal compounds). Nevertheless, the qualitative results of a recent spin-polarized study¹⁷ of the Fe 3s level from clean iron are also consistent with the atomic multiplet theory. We show here that even in the absence of the quantitative theory of spin dependence in core-level photoemission, such spectra can be used in order to provide new information on local magnetic properties in the surface region.

We now proceed with the a study of spin dependence in Fe 3p photoemission of Fe(001) upon interaction with oxygen. The initial exposure to oxygen produces a chemisorbed phase with no change in the Fe 3p spin-integrated or spin-resolved spectra. Such an observation indicates that the oxygen does not effect the magnetic properties of the

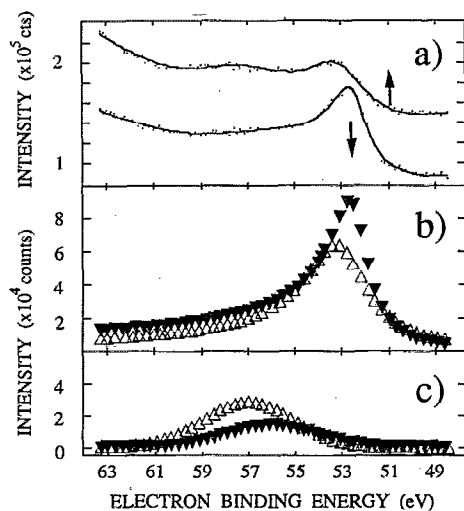


FIG. 3. (a) Spin-resolved Fe 3p spectra, $h\nu = 90$ eV, of the initial iron oxide after exposure to 16 L of O_2 . Also shown (full lines) are curves fitted to each spin component consisting of a Gaussian (for the oxide) and a Doniach-Sunjić line shape plus a background. (b) Majority and minority iron metal components (Doniach-Sunjić line shape) without the background. (c) Majority and minority iron oxide components (Gaussian form) without the background.

surface layer and is consistent with our earlier study⁴ of the valence bands for this system.

Further exposure to oxygen leads to the formation of an oxide layer as evidenced by a chemically shifted core level. The spin-resolved photoemission spectra from this system are shown in Fig. 3(a). Each spin component is fitted to a sum of a Doniach-Sunjić line shape (representing emission from the metal) and a Gaussian peak (representing the oxide) plus a background, also shown. Figures 3(b) and 3(c) show separately these spin-resolved curves fitted to the metal and to the oxide part of the measured spectra, respectively. As expected the spin dependence of the metal remains unchanged [Fig. 3(b)], indicating no detectable change in the magnetic state of the iron substrate. The curves representing the oxide component [Fig. 3(c)], on the other hand, suggest two important observations: First, the oxide component of the 3p spectra has a net polarization, and secondly, its polarization is of the opposite sign (positive) to that of the substrate metal, which remains negative. Thus the new oxide phase clearly possesses a net magnetic moment, which couples antiferromagnetically to the iron substrate below. Figure 3(c) also shows the majority oxide component shifted from the metal peak by 4.5 eV, while the minority component shift is approximately 3.0 eV. It should be noted that the relative binding energy of these two components is reversed from that observed for the clean surface. The atomic picture of multiplet states, however, predicts the lower binding energy peak to have the strongest spectral weight, regardless of the orientation of the magnetic moment. Therefore, the observation of the stronger of the two oxide induced peaks being at higher binding energy cannot be interpreted as an exchange splitting, but more likely indicates the presence of two different chemical states of iron in

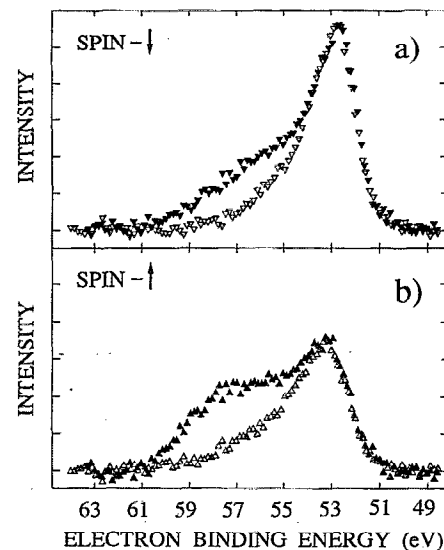


FIG. 4. (a) Minority-spin Fe 3p spectra, $h\nu = 90$ eV, from clean Fe(001) (open triangles) and after exposure to 16 L of O_2 (filled triangles). (b) The same as (a) but for majority-spin electrons.

the initial oxide phase.

The spin-resolved components of this oxide phase can be seen more clearly when they are compared with equivalent spectra from the clean surface, as presented in Fig. 4. In order to highlight the changes in the Fe 3p spectra as a result of oxidation, we show in Fig. 5(a) spin-resolved difference spectra obtained by subtracting the clean surface spectra from the initial oxide one. The binding energies of the substrate iron, Fe^0 , as well as the chemically shifted¹⁸ Fe^{2+} and Fe^{3+} , are indicated. It is evident from Fig. 5(a) that the majority-spin spectrum of the oxide shows the presence of predominantly Fe^{3+} with some contribution

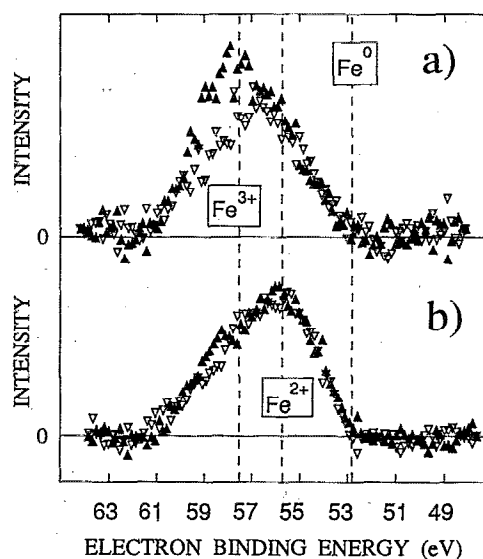


FIG. 5. (a) Spin-resolved Fe 3p spectra of oxide component only after exposure to 16 L of O_2 . (b) The same as (a) but after subsequent annealing to 650 °C.

from Fe^{2+} . The minority spin, on the contrary, indicates the presence of predominantly Fe^{2+} and a small contribution from Fe^{3+} ions. The relative intensity of the majority and minority components is such that there is no net polarization in the Fe^{2+} , and a substantial positive polarization in the Fe^{3+} component of the oxide. There is no majority or minority intensity at the position of the iron metal, which, in this difference spectra, indicates that the magnetization of the iron substrate after the oxidation stays the same.

In Fig. 5(b) we show the spin-resolved difference spectra for the oxygen-exposed surface after annealing to 650 °C. Similar to Fig. 5(a), the metal contributions are subtracted out, suggesting no change in the magnetic state of the substrate. The oxide spectra are now completely unpolarized and shifted approximately 3.0 eV from the clean surface core level. The lack of polarization in this oxide phase may be taken as evidence of either a paramagnetic or antiferromagnetic behavior. It is also evident from this figure that the main contribution to the annealed oxide phase comes in Fe^{2+} form with only a small Fe^{3+} component.

IV. DISCUSSION

The spin analysis in the present study provides important new information on the chemically shifted components. For the initial oxide the Fe^{3+} shows a net polarization whereas the Fe^{2+} component shows no polarization. The opposite order of polarization would be expected for Fe_3O_4 since the Fe^{2+} octahedral sites carry the net moment, whilst the Fe^{3+} ions are split equally between tetrahedral and octahedral sites with their moments canceling each other. The presence of an antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ can also be ruled out on the basis that no polarization would be expected for the Fe^{3+} component. Thus the polarization in the Fe^{3+} component points to the presence of ions with the coordination appropriate to that found in ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3$. Fe^{3+} ions possess a high magnetic moment of $5\mu_B$. This should result in a large exchange-induced splitting for the multiplets in core-level photoemission with, as already noted, the dominant peak at lower binding energy being the spin minority component. This is in fact the component that is observed in the experiment. However, no other exchange split components are observed. This is probably a reflection of the relative intensities of the two components and indeed, earlier spin-integrated Fe 3p photoemission spectra¹⁹ of Fe^{3+} ionic compounds have found that the 5P final states at higher binding energy have much smaller spectral weight as compared to the 7P component.

The initial oxide spectra shown in Fig. 5(a) contains, in addition to the Fe^{3+} peaks (reflecting $\gamma\text{-Fe}_2\text{O}_3$), a smaller unpolarized Fe^{2+} component. This observation indicates the coexistence of an antiferromagnetic Fe_xO phase. Following annealing, the spectra, shown in Fig. 5(b), indicate that the initial oxide converts almost completely to this Fe_xO phase. This is supported by our observation of the unpolarized Fe^{2+} component and is in agree-

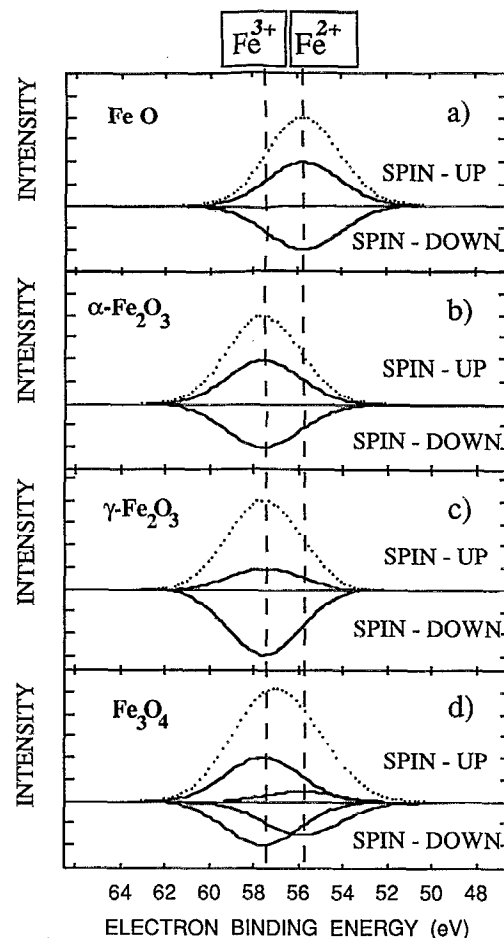


FIG. 6. Spin-resolved Fe 3p spectra expected to be observed from different iron oxides: (a) FeO, (b) $\alpha\text{-Fe}_2\text{O}_3$, (c) $\gamma\text{-Fe}_2\text{O}_3$, (d) Fe_3O_4 . Only the most dominant 7P of the 3p multiplets is included in this simple analysis.

ment with the earlier EELS study.⁸

In summary, we have shown that the combination of core-level shifts (difference in binding energies between Fe^0 , Fe^{2+} , and Fe^{3+} species) and the spin polarization has enabled us to fully characterize the initial oxidation of Fe(001). This is clear from Fig. 6 where we show spin-integrated and spin-resolved Fe 3p spectra expected to be observed for four different iron oxides. In this simple picture we consider only the most dominant 7P component of the 3p multiplets, but the same conclusions would be reached by inclusion of other less pronounced multiplet features. It is clear from Fig. 6 how different oxides or mixtures of oxides can be differentiated, and that spin-resolved spectra obtained in the initial oxidation of Fe(001) are consistent with the presence of a mostly $\gamma\text{-Fe}_2\text{O}_3$ -like oxide with some contribution from Fe_xO -like phase.

In addition of simply adding the chemical analysis of the surface species, the spin analysis of core levels also gives information on the magnetic state of the oxides. We find that initial oxidation forms a mostly ferrimagnetic ($\gamma\text{-Fe}_2\text{O}_3$ -like oxide) phase that couples antiferromagnetically to the iron substrate. This initial oxide represents, however,

only 1–2 atomic monolayers and it is therefore difficult to make a straightforward comparison with the bulk iron oxides. It is more likely that the initial oxide in fact represents a unique oxide phase, as was suggested in the earlier EELS study.⁸ This possibility is confirmed by our observation of an antiparallel alignment of the oxide and the metal substrate moments, an indication of strong coupling between the two. The most obvious way of inducing this antiferromagnetic coupling is a superexchange interaction between the outer Fe^{3+} ions and the substrate atoms mediated by an oxygen ion between. This would suggest that during the initial oxidation, following the chemisorption phase, there is a site reversal of an adsorbate oxygen atom with an underlying iron atom. Lanyon and Trapnell²⁰ have in fact proposed such a site exchange mechanism as the commencement of Mott–Cabrera²¹-type kinetics of the oxidation of iron. Our observation of antiparallel coupling between the oxide and substrate iron moments strongly supports this model.

V. CONCLUSIONS

In this study we have been able to characterize the magnetic properties of the unique iron oxide phase that follows the initial chemisorption stage. This was accomplished by combining photoemission from core levels for chemical selectivity with spin analysis for probing the magnetic properties. In this way it proved possible to distinguish the magnetism of thin oxide layer from the magnetism of the metal substrate despite the fact that both involve the same element. Furthermore, we were able to differentiate between different phases of the oxides. Such a spin-polarized electron spectroscopy for chemical analysis (SPESCA) should prove a useful tool for the examination of local magnetic properties.

ACKNOWLEDGMENTS

We are indebted to Professor A. Arrott and S. D. Bader for the loan of the Fe-picture frame sample. This work was supported in part by U.S. Department of Energy Contract No. DE-AC02-76CH00016 and National Science Foundation Material Research Group Contract No. DMR-86-03304.

- ¹R. Feder, Ed., *Polarized Electrons in Surface Physics* (World Scientific, Singapore, 1985).
- ²J. Kirschner, Ed., *Polarized Electrons at Surfaces*, Vol. 106 in *Springer Tracts in Modern Physics* (Springer, Berlin, 1985).
- ³E. Kisker, K. Schroder, W. Gudat, and M. Campagna, *Phys. Rev. B* **31**, 329 (1985).
- ⁴P. D. Johnson, A. Clarke, N. B. Brookes, S. L. Hulbert, B. Sinkovic, and N. V. Smith, *Phys. Rev. Lett.* **61**, 2257 (1988).
- ⁵E. Kisker, Chap. 12 in Ref. 1.
- ⁶C. R. Brundle, *Surf. Sci.* **66**, 581 (1977).
- ⁷R. Allenspach, M. Taborelli, and M. Landolt, *Phys. Rev. Lett.* **55**, 2599 (1985).
- ⁸Y. Sakisaka, T. Miyano, and M. Onchi, *Phys. Rev. B* **30**, 6849 (1984).
- ⁹J. Unguris, D. T. Pierce, and R. J. Cellota, *Rev. Sci. Instrum.* **57**, 1314 (1986).
- ¹⁰P. D. Johnson, S. L. Hulbert, R. Klaffky, N. B. Brookes, A. Clarke, B. Sinkovic, and M. Kelly (to be published).
- ¹¹We are indebted to A. Arrott and S. Bader for the loan of this sample.
- ¹²S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).
- ¹³C. Carbone and E. Kisker, *Solid State Comm.* **65**, 1107 (1988).
- ¹⁴C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Lett.* **23**, 1397 (1969).
- ¹⁵T. Yamaguchi, S. Shibuya, and S. Sugano, *J. Phys. C* **15**, 2625 (1982).
- ¹⁶G. M. Rothberg, *J. Magn. Magn. Mater.* **15–18**, 323 (1980).
- ¹⁷F. U. Hillebrecht, R. Jungblut, and E. Kisker, *Phys. Rev. Lett.* **65**, 2450 (1990).
- ¹⁸C. R. Brundle, T. J. Chuang, and K. Wandelt, *Surf. Sci.* **68**, 459 (1977).
- ¹⁹S. P. Kowalczyk, Ph. D. thesis, University of California, Berkeley Report No. LBL-4319, 1976.
- ²⁰M. A. Lanyon and B. M. Trapnell, *Proc. R. Soc. London Ser. A* **277**, 3875 (1955).
- ²¹N. Cabrera and N. F. Mott, *Rep. Prog. Phys.* **12**, 163 (1948).